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(54) Title of the Invention: Forming method of thin film

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Specification

1. Title of the Invention

Forming method of thin film

2. Scope of Claim

1. A method of forming a thin film by using plasma and light, comprising the steps of:

introducing halogen gas into a deposition chamber where a base body is set,

exciting the halogen gas and treating the base body, as a halogen treatment,

introducing a first gas that is not deposited by itself even when excited, into a reaction vessel where the base body is set, after the halogen treatment,

plasma-exciting the first gas that is introduced into the reaction vessel, and

introducing a second gas into the reaction vessel so that it reacts with the first gas that is excited, attaching a reaction product to the base body, and irradiating the base body with the reaction product attached with light.

2. A method of forming a thin film by using plasma and light, comprising the steps of:

introducing halogen gas into a deposition chamber where a base body is set,

exciting the halogen gas and treating the base body, as a halogen treatment,

introducing a first gas that is not deposited by itself even when excited, into a reaction vessel where the base body is set, after the halogen treatment,

plasma-exciting the first gas that is introduced into the reaction vessel,

exposing the base body after the halogen treatment to the first gas that is excited, and

introducing a second gas into the reaction vessel so that it reacts with the first gas that is excited, attaching a reaction product produced to the base body, and irradiating the base body with the reaction product attached with light.

3. Detailed Description of the Invention

[Field of the Industrial Application]

The present invention relates to a method of forming a thin film, more specifically, to a method of forming an insulating film of a semiconductor device, and especially to a method of forming an insulating film that can be used suitably for a field-effect transistor.

[Conventional Technology]

Conventionally, a gate insulating film of a MOSFET using single crystal silicon is formed generally by heating single crystal silicon to 900 to 1100 °C in oxygen

atmosphere. Further, a gate insulating film of a MISFET such as InP, GaAs and the like or of a TFT whose semiconductor layer comprises amorphous silicon (hereinafter referred to as a-Si) or polycrystalline silicon is generally formed by sputtering, thermal CVD, plasma CVD or the like.

[Problem to be solved by the Invention]

In the case where a semiconductor device is manufactured three-dimensionally, like the case where a MOSFET of SOI structure is applied to a semiconductor device of three-dimensional structure, however, a plurality of semiconductor layers are formed. Therefore, when a device in upper layer is formed by using heat energy, underlying semiconductor layers may be damaged by the heat.

Further, also in the case of a device using polycrystalline Si or single crystal Si on a glass, the glass substrate suffers damage by heat, so that it is difficult to use thermal oxidation method for forming a gate insulating film.

In addition, in the case where sputtering or plasma CVD is used as a gate insulating film, damage is caused on a semiconductor layer by accelerated ions, and interface state between the semiconductor layer and an insulating film increases, which sometimes causes deterioration in mobility of carriers that leads to deterioration in device performance.

[Object]

It is an object of the present invention to propose a method of forming a thin film that can drastically improve device performance compared to the conventional one.

Further, it is an object of the present invention to propose a method of forming a thin film that can reduce interface state between a semiconductor layer and an insulating film.

In addition, it is an object of the present invention to propose a method of forming a thin film that can reduce interface state between a semiconductor layer and an insulating film by performing a pretreatment on a base body.

[Means for Solving the Problem]

The present invention was accomplished by concentrated and repeated research work for solving the problem of the conventional technology. A method of forming a thin film of the present invention is a method of forming a film by using plasma and light, and comprises the steps of: introducing halogen gas into a deposition chamber where a base body is set; exciting the halogen gas and treating the base body, as a halogen treatment; introducing a first gas that is not deposited by itself even when excited, into a reaction vessel where the base body is set, after the halogen treatment; plasma-exciting the first gas that is introduced into the reaction vessel; and introducing

a second gas into the reaction vessel so that it reacts with the first gas that is excited, attaching a reaction product produced to the base body, and irradiating the base body with the reaction product attached with light. Or, the present invention is a method of forming a film by using plasma and light, and comprises the steps of: introducing halogen gas into a deposition chamber where a base body is set; exciting the halogen gas and treating the base body, as a halogen treatment; introducing a first gas that is not deposited by itself even when excited, into a reaction vessel where the base body is set, after the halogen treatment; plasma-exciting the first gas that is introduced into the reaction vessel; exposing the base body after the halogen treatment to the first gas that is excited; and introducing a second gas into the reaction vessel so that it reacts with the first gas that is excited, attaching a reaction product produced to the base body, and irradiating the base body with the reaction product attached with light.

[Function]

According to the present invention, interface state density between a base body surface and a semiconductor can be drastically reduced by performing a halogen treatment as a pretreatment on a base body surface where a film is deposited, or by performing a treatment by a first gas following the halogen treatment. Further, the treatment can be performed under low temperature by employing a method of forming a film using plasma and light. By using the same light source and plasma source as the ones used for film formation, the pretreatment can be performed more effectively. It is preferable especially for the halogen treatment that the treatment can be performed under low temperature.

In the present invention, the reason why interface state density is reduced by the pretreatment using halogen gas or by a pretreatment using the first gas performed following the halogen gas is considered to be due to the mechanism described hereinafter.

Generally, Si base body to be used when manufacturing a semiconductor device is etched using hydrofluoric acid (HF) solution as etching solution and then cleaned by ultrapure water, in terms of impurity removal. It is known that a dangling bond of Si on the base body surface is terminated by hydrogen atoms and not easily oxidized. Therefore, in the case where a SiO_2 film is formed by CVD on this surface, for example, it is difficult for Si and oxygen to be bonded directly because Si-H bonds exist on the base body surface. Accordingly, it is thought that defective reaction arises on the base body surface, many Si-H bonds remain in the interface, and a Si-OH bond and the like is formed and the interface state density becomes high. In response to these, by treating a Si wafer by excitation species of halogen atoms such as F for

example, H of Si-H bond in the interface can be effectively substituted with F, and hydrogen can be removed. The substitution between O and F of Si-F bond occurs more easily than substitution between H and O. Therefore, the substitution between F and O is conducted by performing a treatment of exposing the base body to excitation species of oxygen as a first gas used when a SiO_2 film is formed (which excitation species of oxygen are obtained by plasma excitation and/or light excitation), so that Si-O bonds that are more favorable and stable can be obtained. As above, interface state density between Si and a SiO_2 film can be reduced by effectively making the bonds between Si and O on the base body surface.

[Embodiment]

According to the present invention, when an insulating film is formed on a base body of semiconductor, a treatment using halogen gas excited by light or plasma is performed as a pretreatment before the film formation. And/or, following this gas treatment, by performing a treatment using a first gas that is excited, interface state density at the base body interface is reduced.

Further, by employing a method of forming a film by light and plasma, a base body is treated under low temperature that is suitable for performing a halogen gas treatment. In addition, by using either of plasma source that excites the first gas when forming a film or light with which the base body is irradiated, an apparatus for film formation can be simplified.

Further, when a treatment by halogen gas is performed, desorption of hydrogen is accelerated and interfusion of hydrogen that causes fluctuation of threshold electrode (sic) is prevented by light irradiation, and a dense film can be formed. As for the gas treatment by the first gas, in addition, the substitution between the first gas species and halogen can be conducted effectively by plasma-exciting the gas or light irradiation.

An example of an apparatus for film formation that can be used suitably to perform a method of forming a thin film of the present invention will be described hereinafter with reference to Fig. 1.

In Fig. 1, reference number 1 is an electrode, and 2 is a reaction vessel functioning as another electrode also. As shown in Fig. 1, the reaction vessel 2 is grounded. Reference number 3 is a base body, and the examples of it include a semiconductor such as silicon, a compound semiconductor such as GaAs, or a base body wherein a semiconductor layer such as single crystal Si, polycrystalline Si and amorphous silicon is deposited on an insulating substrate (a substrate comprising insulating material, or a substrate whose surface is insulated).

Each of 4a, 4b and 4c is a gas-feed port. The gas-feed ports 4a and 4b are

located in the upper part of the reaction vessel 2 and set close to the electrode 1. A gas 10a that includes halogen is introduced through the gas-feed port 4a into a deposition chamber, and a first gas 10b is introduced through the gas-feed port 4b. Diluted gas of halogen such as F_2, Cl_2, Br_2 diluted by inert gas such as He and Ar, or the gas that includes halogenated compound such as HF, HCl, HBr, NF_3 and SF_6 can be cited as the gas 10a that includes halogen.

The gas that includes nitrogen atoms, and the gas that includes oxygen atoms can be cited as the first gas. In the present invention, in the case where a pretreatment using the first gas is performed, hydrogen content in a film to be formed can be drastically reduced, compared to the case where a film is formed using diode parallel plate plasma enhanced CVD.

The gas-feed port 4c is placed in the under side opposite to the electrode 1, and a second gas 10c is introduced through this gas-feed port 4c. The gas such as SiH_4 and Si_2H_6 that include Si, or organic oxysilane material such as TEOS ($(C_2H_5O)_4Si$) can be cited as the second gas.

Reference number 5 is a power supply that applies a voltage between the reaction vessel 2 and the electrode 1 to generate plasma. Plasma can be generated by means of high frequency wave, microwave or magnet, or combinations of these.

The pressure (operation pressure) of the inside of the reaction vessel during film formation is preferably 10 to 500 mTorr.

As for the foregoing method of forming a thin film, in order to prevent plasma damage further and enlarge a base body area, it is preferable to set the electrode area of a plasma source not more than 1/10 of the area of the inner wall of the reaction vessel. It is preferably 0.02 to 0.06, and more preferably, 0.04 to 0.05. In this way, if the electrode area is smaller than the inner wall area of the reaction vessel and a voltage is applied between the electrode and the reaction vessel, plasma intensity is large near the electrode, and smaller near the base body. As a result, damage to the base body or film can be reduced.

Reference number 6 is a light source, and the examples of it include lamps such as a Hg lamp, a Xe lamp, a Xe-Hg lamp, a W lamp and a halogen lamp, or lasers such as a N_2 laser, an Ar laser, a YAG laser and an exima laser of a CO_2 laser. Of course other light than the above may be used, and especially one that is not easily absorbed by introduced gas but absorbed by reaction intermediate during film formation and by halogen gas may be used. By using at least either of the plasma source for exciting the first gas when forming a film and the light with which a base body is irradiated, as the light source or plasma source to be used when exciting halogen gas, the apparatus is

simplified and a pretreatment on a base body and film formation process can be performed in succession. The procedures for forming a thin film by using this apparatus will be described hereinafter.

A base body is set in a vacuum vessel 2 and the inside of the reaction vessel 2 is depressurized to the intended pressure, then the halogen gas 10a for a pretreatment is introduced and the operation pressure is kept to the intended value. At that time, the base body 1 is irradiated with light from the light source 6, or a voltage is applied between the electrode 1 and the reaction vessel 2 for plasma-excitation, or both of the two are performed. In the case where infrared light or light containing infrared light is used as light for irradiation, the temperature of the base body can be set to be the intended value by the light irradiation. In the case where light that cannot raise the temperature of the base body is used, a heater may be placed on a base body holder to set the temperature to be the intended value.

A halogen pretreatment is performed under the above-mentioned condition. After that, halogen gas is removed by evacuating the inside of the reaction vessel to high vacuum. When a treatment by a first gas is performed in succession, oxygen or nitrogen as the first gas is introduced into the reaction vessel, and the operation pressure is set to be the intended value. In this case, in the same way as the case of the halogen pretreatment, it is good to irradiate the base body 1 with light from the light source 6 or apply a voltage between the electrode 1 and the reaction vessel 2 for plasma-excitation, or perform both of the two. The pretreatment by the first gas can be performed under the above-mentioned condition.

Next, the inside of the reaction vessel 2 is vacuum-evacuated again to the intended pressure. After that, the first gas 10b is flown through the gas-feed port 4c into the reaction vessel 2, and this first gas is plasma-excited. The second gas 10c is introduced through the gas-feed port 4c into the reaction vessel 2, and reacted with the excited first gas setting the gas pressure to be the prescribed value. Plasma can be generated by applying a high-frequency voltage of 13.56 MHz, for example, between a capacity coupling type electrode 1 and the reaction vessel 2. At this time, the base body 1 is irradiated with light from the light source, and film formation is performed. Here, although a light source that is different from the one used for the pretreatment may be used as the light source to perform the light irradiation, the apparatus can be simplified by using the same light source.

Embodiment 1

The preferred embodiment of the present invention will be described more

specifically hereinafter.

A Si single crystal wafer as a base body is placed in the inside of the reaction vessel 2, and the inside of the reaction vessel 2 is vacuum-evacuated to 1×10^{-7} Torr by a vacuum evacuation apparatus. After that, 5 sccm of F_2 diluted to 5 % by He is introduced as a halogen gas 10a for a pretreatment, and the operation pressure is kept to 100 mTorr. On the other hand, the base body 1 is irradiated with Xe lamp light of 0.6 W/cm^2 from the light source 6. By this irradiation, the substrate temperature is kept to 300 °C, and the pretreatment is performed for 5 minutes under the above-mentioned condition.

Next, the inside of the reaction vessel 2 is vacuum-evacuated again to 1×10^{-7} Torr. Oxygen gas is used as a first gas 10b, and monosilane gas is used as a second gas 10c. First, the first gas 10b is flown through the gas-feed port 4b into the reaction vessel 2 at the rate of 100 sccm, and this first gas is plasma-excited. The second gas 10c is introduced through the gas-feed port 4c into the reaction vessel 2 at the rate of 5 sccm, and the operation pressure of this time is set to be 100 mTorr. Plasma is generated by applying 100 W of high-frequency voltage of 13.56 MHz between the capacity coupling type electrode 1 and the reaction vessel 2. Electron density of this time is 8×10^7/cm^3. In the same way as the case of the pretreatment, the base body 1 is irradiated with light of 0.6 W/cm^2 from the light source 6.

When deposition is performed under the above-mentioned condition for 3 minutes, 1000 ± 25 Å (angstrom) of SiO_2 film is formed. That is to say, variation in the film thickness is about ± 2.5 %, which is small.

The silicon dioxide film formed in the above-mentioned way is evaluated as below.

[1] Refractive index: 1.44 to 1.46, which is about the same as that of a thermally-oxidized film.

[2] Infrared spectroscopic characteristic: Absorption by the bond of Si-H and S-OH is not found but only absorption by Si-O bond is found.

[3] Electrical characteristic: Dielectric constant is 4.1, withstand voltage is 10 MV/cm, and interface state density between the semiconductor and the insulating film (hereinafter referred to as interface state density) is 5×10^{10} eV^{-1} cm^{-2}.

As the above, a film with good characteristics can be formed.

Embodiment 2

After the inside of the reaction vessel 2 is vacuum-evacuated in the same way as the embodiment 1, 5 sccm of He-F_2 5 % gas 10a is introduced through the feed port

4a into the vacuum reaction vessel. Then the Xe lamp irradiation is performed, keeping the operation pressure at 100 mTorr, and the pretreatment is performed for 5 minutes.

Next, F_2 in the reaction vessel is removed by evacuating the inside of the vessel 2 to high vacuum, and 100 sccm of oxygen that is the first gas is introduced, and the operation pressure is set to be 100 mTorr. Also at this time, irradiation of light of 0.6 W/cm^2 from the light source 6 is performed, and oxygen treatment is performed for 5 minutes.

Next, 5 sccm of SiH_4 as the second gas is introduced through the gas-feed port 4c into the reaction vessel, the operation pressure is set to be 100 mTorr, and oxygen that is the first gas is excited by plasma. The deposition rate film thickness distribution, refractive index, infrared spectroscopic characteristic, dielectric constant and withstand voltage of SiO_2 film that is formed under the above-mentioned condition are favorable, as is the case with the embodiment 1. In addition, the interface state density is 2×10^{10} eV^{-1} cm^{-2}, which is even smaller, and the advantageous effect of the oxygen treatment can be seen.

Embodiment 3

After the inside of the reaction vessel is vacuum-evacuated in the same way as the embodiment 1, He-NF_3 5 % gas is introduced through the feed port 4a into the reaction vessel at the rate of 5 sccm. Then, the operation pressure is set to be 100 mTorr, and the gas is plasma-excited. The pretreatment is performed under the above-mentioned condition for 5 minutes.

After that, NF_3 in the reaction vessel is removed by evacuating the inside of the reaction vessel to high vacuum again, and the first gas (O_2) is introduced through the feed port 4b. Then the operation pressure is set to be 100 mTorr, and the oxygen treatment is performed for 5 minutes by plasma-exciting the oxygen. Next, SiH_4 as the second gas is introduced through the gas-feed port 4c into the reaction vessel at the rate of 5 sccm. The operation pressure is set to be 100 mTorr. And a film is formed by irradiating the base body with light from the light source 6 at the same time as exciting oxygen that is the first gas by plasma.

The deposition rate film thickness distribution, refractive index, infrared spectroscopic characteristic, dielectric constant and withstand voltage of SiO_2 film that is formed under the above-mentioned condition are favorable, as is the case with the embodiment 1. In addition, the interface state density is 1×10^{10} eV^{-1} cm^{-2}.

Embodiment 4

After the inside of the reaction vessel 2 is vacuum-evacuated in the same way as the embodiment 1, He-NF_3 5 % gas is introduced through the feed port 4a into the reaction vessel at the rate of 5 sccm. Then, setting the operation pressure to be 100 mTorr, the gas is plasma-excited, and at the same time, irradiation of light of 0.6 W/cm^2 from the light source 6 is performed. After that, NF_3 in the reaction vessel is removed by evacuating the inside of the reaction vessel to high vacuum again, and the first gas (O_2) is introduced through the feed port 4b, then the operation pressure is set to be 100 mTorr. And the base body is irradiated with light from the light source 6 at the same time as exciting the oxygen by plasma, and the oxygen treatment is performed.

Next, SiH_4 as the second gas is introduced through the gas-feed port 4c into the reaction vessel at the rate of 5 sccm, and the operation pressure is set to be 100 mTorr. And a film is formed by irradiating the base body with light from the light source 6 at the same time as exciting oxygen that is the first gas by plasma.

The deposition rate, refractive index, infrared spectroscopic characteristic, dielectric constant and withstand voltage of SiO_2 that is formed under the above-mentioned condition are favorable, as is the case with the embodiment 1. In addition, the interface state density can be decreased to 5×10^9 eV^{-1} cm^{-2}.

[Effect of the Invention]

According to the present invention, [1] plasma damage to a base body can be reduced, because the base body can be placed away from the part with greatest intensity of plasma. In addition, by performing a pretreatment using excited halogen gas or/and a treatment using excited first gas (oxygen treatment and nitrogen treatment), the interface state density can be drastically reduced, and a film with favorable electrical characteristic can be formed.

[2] By using at least either one of the plasma source that is used for exciting the first reactive gas when a film is formed, and the light source for irradiating a base body, to excite the aforesaid halogen gas, the apparatus is simplified, and a film formation process can be performed in succession.

[3] A film that is close to stoichiometric composition can be formed.

[4] A film with small hydrogen content can be formed, and the fluctuation of threshold voltage can be prevented.

4. Brief Description of the Drawings

Fig. 1 is a conceptual diagram showing an apparatus related to the

embodiments of the present invention.

1: electrode

2: reaction vessel

3: base body

4a, 4b and 4c: gas-feed port

5: plasma generating means

6: light source

10a, 10b and 10c: material gas